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A new electron gas model for lattice vibrations in metals I : development of the model.

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The theoretical study of the lattice dynamics of metals is generally based on either the phenomenological force constant method or the pseudopotential method. However, it has been found that all the existing phenomenological models are inconsistent. In particular, the most widely used Sharma-Joshi model contains physical and mathematical inconsistencies. Hence a new model based on the deformation potential approximation has been developed. By comparing this model with the existing models, its salient features and limitations are discussed.

1. INTRODUCTION

The wealth of lattice dynamical data that has ensued from experiments using the inelastic scattering of neutrons from crystals remain largely unexplained. This is particularly so in the case of the transition metals. The difficulty in developing a general theory of lattice vibrations in metals is that the metal is a many-body system and the interaction of the constituent nuclei and electrons is very intricate. Therefore, two independent schemes of approximation have been in use. One of them is purely phenomenological. In this scheme, the interaction between the lattice particles is simulated by means of force constants. The metal is envisaged as a lattice of ions over which is superimposed the highly mobile conduction electron gas. The force that sustains the vibration of any lattice ion is the sum of the forces exerted by a relatively few neighbouring ions and the force due to the electron gas. The latter has been termed as *volume forces*. In the other method, the total interaction is divided into three parts, the Coulomb interaction between the bare ions, the ion core overlap interaction and the electron-ion interaction. The electron-ion interaction is described in terms of the pseudopotential. The former method is very general as it involves no assumptions regarding the actual interactions between the particles. Hence it is applicable to any metal. The latter method is of limited applicability as it can be effectively utilized only in those cases where a pseudopotential can be devised.

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It is necessary to have a good phenomenological theory which is often a forerunner to more exact calculations Unfortunately, no consistent theory has been developed so far, mainly because of the difficulties involved in the proper evaluation of the effect of the conduction electrons. The early theory of de Launay (1956) contained the crude assumption that the conduction electrons constitute an elastic gas Bhatia (1955) took account of the quantum nature of the electron gas partly. But the theory failed to satisfy the requirements of lattice symmetry. There have been a few unsatisfactory attempts (Krebs 1965, Bajpai 1972) to improve Bhatia's elementary theory by devising arbitrary mathematical procedures to satisfy the symmetry requirements of the lattice. The most successful among the phenomenological methods is that of Sharma & Joshi (1963) As in the de Launay model the conduction electrons are assumed to behave like classical particles The strain energy of the electron gas due to the passage of a lattice wave gives rise to volume forces. This model has been used very extensively till to-day (Neelakandan 1974) in spite of the fact that it contains serious physical and mathematical inconsistencies. A physical inconsistency is that the electrons which are assumed to be classical particles with no interactions among them, possess *volume-dependent* strain energy. More serious is a mathematical inconsistency in the evaluation of the strain energy given by

$$\Phi_e = \tfrac{1}{2} K_e \int \chi^2(\mathbf{r}) d\tau \tag{1}$$

where K_e is the bulk modulus of the electron gas, $\chi(\mathbf{r})$ the strain at the point $\mathbf{r}$ and the integration being over the whole crystal volume. Instead of averaging the expression for square of the strain and integrating, these authors integrated the square of the average strain. These deficiencies of the model have remained unquestioned for over a decade, largely because of the success of the model in explaining the lattice vibrational properties of several metals.

Thus, it is found that none of the existing phenomenological schemes gives a consistent account of the effect of the electron gas This paper describes the development of a consistent model for volume forces in metals. The new electron gas model based on the deformation potential approximation is described and the expression for volume forces is deduced in section 2. A detailed discussion and comparison of this model with others are presented in section 3 and conclusions are summarized in section 4. The validity of this model has been established by studying the lattice vibrational properties of alkali metals and noble metals and these will form the subject matter of subsequent papers.

2. The Model

The metal is assumed to consist of a lattice of point ions embedded in the electron gas. The potential felt by the conduction electrons, in the absence of

lattice vibrations, is zero. During lattice vibrations, this potential fluctuates sinusoidally However, the fluctuations are of comparatively longer wave length than the de Broglie wave length of the electrons at the Fermi surface Consequently, the electrons are still distributed in free electron states and the Fermi level is maintained constant. This is the Thomas-Fermi approximation.

The general expression for the displacement at any point in the medium is

$$\boldsymbol{u}(\boldsymbol{r}) = \boldsymbol{\alpha}_q A_q \exp\left[i\{(\boldsymbol{q},\boldsymbol{r}.)-\omega_q t\}\right] \tag{2}$$

where $\boldsymbol{\alpha}_q$ is a unit vector in the direction of the amplitude A_q, ω_q is the frequency corresponding to the wave vector $\boldsymbol{q} = 2\pi/\lambda$ and t is time. The compressive strain at any point is given by

$$\chi(\boldsymbol{r}) = -\nabla\, \boldsymbol{u}(\boldsymbol{r}) = -iq[\boldsymbol{\xi}\, \boldsymbol{u}(\boldsymbol{r})] \quad \ldots \quad (3)$$

where $\boldsymbol{\xi}$ is a unit vector in the direction of the wave vector. The expression for the dilatational strain would appear with a positive sign In the adiabatic approximation, there is no phase lag between the motion of the ions and the electrons Hence, the strain in the ion lattice and the electron gas can be represented by eq (3). However, for the strain in the ion lattice, $\boldsymbol{r}$ is replaced by the lattice vector $\boldsymbol{L}$ since there is no physical significance for lattice strain in the interstices of the lattice The idea is that one can still join the displaced positions of the ions by a smooth curve of the form given by eq. (3). In the adiabatic approximation, one can consider the electron distribution by imagining that the lattice of the ions is frozen at any instant during its vibration and the expression for the strain can be written, by ignoring the time part in eq. (3) as

$$\chi(\boldsymbol{r}) = -iA_q q(\boldsymbol{\alpha}_q\, \boldsymbol{\xi})\exp(i\boldsymbol{q}\, \boldsymbol{r}) \quad \ldots \quad (4)$$

In the compressed regions of the lattice, the potential energy is supposed to be changed in the same sinusoidal fashion as the strain The potential energy is more negative, let this be denoted by $U^+(\boldsymbol{r})$ The change in potential energy can be assumed to be proportional to the strain and given by

$$U^+(\boldsymbol{r}) = \eta\chi(\boldsymbol{r}) \quad \ldots \quad (5)$$

More electrons rush into this region in order to lower their energies and to establish charge neutrality with the increased density of ions (adiabatic screening). This makes the Fermi level more positive the magnitude of the shift being

$$\frac{n_0\chi(\boldsymbol{r})}{D(E_F{}^0)} \tag{6}$$

where n_0 is the equilibrium electron density and $D(E_F{}^0)$ the density of states at the Fermi level The new Fermi energy is given by

$$E_F{}'(\boldsymbol{r}) = E_F{}^0 + \frac{n_0\chi(\boldsymbol{r})}{D(E_F{}^0)} \tag{7}$$

Recalling that $D(E_F^0) = 3n_0/2E_F^0$, one gets

$$E_F'(\mathbf{r}) = E_F^0[1 + \tfrac{2}{3}\chi(\mathbf{r})] \quad \ldots (8)$$

In the compressed regions of the electron gas, the electron density is more than its equilibrium value. The resulting increase in the electron-electron interaction manifests itself as an increase in the kinetic energy of the electrons. Consequently, the wave vector of each electron increases. Thus the labelling of the states in the compressed region gets altered This constitutes a change in the Fermi level which, for any arbitrary shape of the Fermi surface, is given by (Ziman 1960)

$$\delta E_F'(\mathbf{r}) = \frac{v_F}{s} \int \frac{\eta\chi(\mathbf{r})}{v_K}\, ds \quad \ldots (9)$$

where v_F and v_K are the velocities of electrons at the Fermi surface and any state K and ds is the elemental area on the Fermi surface. For a spherically symmetric Fermi surface, it can be shown that the wave number of the electron is changed from K to K', the two being related by

$$K' = K[1 + \tfrac{1}{3}\chi(\mathbf{r})] \quad \ldots (10)$$

Correspondingly, the Fermi energy given by eq. (8) is changed to

$$E_F(\mathbf{r}) - E_F'(\mathbf{r})[1 + \tfrac{1}{3}\chi(\mathbf{r})]^2 \simeq E_F^0[1 + \tfrac{4}{3}\chi(\mathbf{r})] \quad \ldots (11)$$

Because of the change in the Fermi energy, the average energy of an electron changes. Thus, the new value of the average energy is

$$E > = \eta\chi(\mathbf{r}) + \tfrac{3}{5}E_F^0[1 + \tfrac{4}{3}\chi(\mathbf{r})] \quad (12)$$

The total energy of the system with N electrons is $N < E >$. The cohesive energy of a simple metal like sodium is purely electronic It should be minimum when the ions are at their equilibrium positions (Nabarro 1967). Therefore, the total energy $N < E >$ has to be a minimum when the system is free of strain, that is, when

$$\left[\frac{d(N<E>)}{d\chi(\mathbf{r})}\right]_0 = 0 \quad (13)$$

This gives the value of the constant η as

$$\eta = -\tfrac{4}{5}E_F^0. \quad \ldots (14)$$

The total energy of an electron at the Fermi level is the sum of eqs. (5) and (11) and the total change in the energy is given by

$$\delta E_F(\mathbf{r}) = \tfrac{8}{15} E_F^0\chi(\mathbf{r}). \quad \ldots (15)$$

Thus, the change in the Fermi energy due to the adiabatic screening and the expansion of the band system is more than what is necessary to compensate the change in the potential energy. This means the Fermi energy in the compressed region is more than its equilibrium value, while in the dilated region it is less. Such an oscillation in the Fermi level is not permitted as it is a chemical potential. For the Fermi level to stay flat, the potential energy of the electrons redistributes such that an electron has a potential energy given by

$$U(\boldsymbol{r}) = -\left(\tfrac{8}{15}\right) E_F{}^0 \chi(\boldsymbol{r}) \qquad \ldots \quad (16)$$

in the compressed region. This is known as the *deformation potential*.

The deformation potential given by eq. (16) corresponds to the adiabatic approximation under which the maximum energy of an electron remains constant, but its average energy still has large variations in the metal. If the electrons are allowed to redistribute and minimize their energy, the deformation potential is slightly reduced and this corresponds to the equilibrium situation. Allowance for the redistribution can be made by letting a few electrons at the Fermi level in the compressed region to flow back into the dilated region. This will modify the deformation potential (Ziman 1960) to

$$U(\boldsymbol{r}) = \frac{-\left(\tfrac{8}{15}\right) E_F{}^0 \chi(\boldsymbol{r})}{1+(q^2/k_{TF}{}^2)} \qquad \ldots \quad (17)$$

where $k_{TF}{}^{-1}$ is the Thomas-Fermi screening length given by

$$k_{TF}{}^2 = 4\pi e^2 \left(\frac{3n_0}{2E_F{}^0} \right) \qquad \ldots \quad (18)$$

Since both $U(\boldsymbol{r})$ and $\chi(\boldsymbol{r})$ have the same periodicity, the Fourier transform of $U(\boldsymbol{r})$ can be written as

$$U(\boldsymbol{q}) = \frac{-\left(\tfrac{4}{5}\right) \left(\frac{4\pi n_0 e^2}{q^2} \right)}{1+(k_{TF}{}^2/q^2)} \qquad \ldots \quad (19)$$

The electrostatic fields due to the sinusoidal potential given by eq. (17) give rise to volume forces. An expression for the volume forces can readily be derived (Bhatia 1955). Substituting for $\chi(\boldsymbol{r})$ in eq. (17) from (4) and taking the gradient, one gets for volume forces

$$\boldsymbol{F}(\boldsymbol{r}) = -\xi A_q q^2 (\boldsymbol{\alpha}_q, \xi) \frac{\left(\tfrac{8}{15}\right) E_F{}^0}{1+(q^2/k_{TF}{}^2)} \exp(i\boldsymbol{q}.\boldsymbol{r}) \qquad \ldots \quad (20)$$

For the electron gas, the continuum model has been used. Hence there is deformation at every point in the medium. In contrast, the point ion model

allows deformation of the lattice only at the lattice points The deformation of the electron gas adjoining a particular ion can be thought to be produced by the motion of the ion. Hence, the deformation potential of the electron gas in a certain region surrounding the ion is assumed to provide a restoring force on the ion. The best way to consider the effect is to think that the crystal is partitioned into Wigner-Seitz polyhedral cells and consider that the deformation potential of the electron gas in a cell contributes the restoring force on the enclosed ion. One can calculate the average deformation potential in the polyhedral cell and determine the resulting force Alternatively one can calculate the average force in the polyhedral cell. The latter is mathematically easier. Thus the average force can be found as

$$<\boldsymbol{F}(\boldsymbol{r})> = -\xi A_q\, q^2(\boldsymbol{\alpha}_q.\boldsymbol{\xi})\, \frac{(\frac{5}{12})E_F^0}{1+(q^2/k_{TF}^2)}\, S(\boldsymbol{q}) \qquad \ldots (21)$$

where $S(\boldsymbol{q})$ is defined by

$$S(\boldsymbol{q}) = \frac{\int_{\Omega} \exp(i\boldsymbol{q}.\boldsymbol{r})d\tau}{\Omega} \qquad \ldots (22)$$

and Ω is the volume of the polyhedral cell. The integral in eq (22) has to be evaluated for the actual shape of the polyhedral cell which is, in general, quite complex. It has been customary to approximate it to a sphere. The integral in eq. (22) can then be evaluated quite easily to obtain

$$\frac{\int_{\Omega} \exp(i\boldsymbol{q}\,\boldsymbol{r})d\tau}{\Omega} = 3\left[\frac{\sin(qr_0)-(qr_0)\cos(qr_0)}{(qr_0)^3}\right] - G(qr_0) \qquad \ldots (23)$$

where r_0 is the radius of the equivalent sphere The replacement of the polyhedral cells by spheres, according to Wilson (1954) *makes the energy a function of the atomic volume only and not of the type of crystal structure* The function $G(qr_0)$ is insensitive to the symmetry of the lattice. To take account of the symmetry, the integral in eq (22) is evaluated for the actual shape of the polyhedral cell. The method and the relevant expressions are given elsewhere (Neelakandan 1974).

3 Discussion

3 1 *Nature of the volume forces*

A proper description of volume forces in metals should explain the correct variation of the force with $\boldsymbol{q}$ of lattice vibrations, especially the fact that the effect of the electron gas becomes negligibly small or vanishes altogether for wave vectors near Brillouin zone boundaries, in order to meet the symmetry requirements of the lattice. The most significant term in the expression for

the volume forces in the present model is the interference factor, $S(q)$ and its variation with the dimensionless parameter, $\zeta = q/q_{max}$ is shown in figure 1. For comparison, the interference factor $G(qr_0)$ is also plotted alongside. The deformation potential which is responsible for the volume forces is negative in

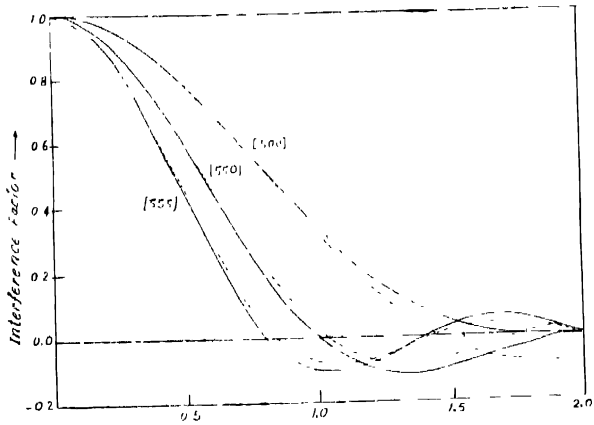

Fig. 1. ζ-dependence of the interference factor along the principal symmetry directions of the b c c. structure. Full line corresponds to $S(q)$ and broken line corresponds to $G(qr_0)$.

the compressed region and positive in the dilated region. The mean value of the force depends on the extent to which opposing forces in the compressed and dilated regions cancel each other, this is, in turn, determined by the wave vector q. For very small values of q, the forces inside the Wigner-Seitz cell are all of the same sign (positive, say) and the interference factor which represents the normalized average of forces is unity As the value of q gradually increases, $S(q)$ decreases, firstly because the forces all over the cell are not equal, secondly as a consequence of the appearance of the negative forces in the dilated regions. For still larger values of q the cancellation of opposing forces becomes more effective and $S(q)$ rapidly decreases. When q corresponds to the first reciprocal lattice vector, the compressed and dilated regions are equal and hence the interference factor reduces to zero. On the contrary $G(qr_0)$ does not pass through zero because the corresponding wavelength is not exactly equal to the cell dimensions in that direction.

3.2. *Comparison with other force constant models*

Since all electron gas models exhibit intrinsic q^2 dependence of the volume

forces, F/q^2 is denoted by a parameter Θ and its variation with ζ for various models is shown in figure 2. For instance in the Bhatia model (1955)

$$\Theta_B = \frac{1}{1+(q^2/k_{TF}^2)} \qquad \ldots \quad (24)$$

while in the present model

$$\Theta_R = \Theta_B S(q). \qquad (25)$$

As a consequence of averaging the force in the Wigner-Seitz cell Θ_R decreases faster than Θ_B. In the Bhatia model the force on the ion is supposed to be that acting at the lattice point. The deformations of the electron gas and the consequent volume forces in the interstices of the lattice are ignored. This is inconsistent with its own assumption of the continuum model of the ionic and the electronic media. In addition, it is assumed there that the volume forces are entirely the result of the redistribution of a few electrons at the Fermi level. Thus there would be no forces in the adiabatic approximation (see the lower horizontal line in figure 2).

Assuming that the strain in the electron gas is equal to that in the ion lattice under adiabatic approximation, Sharma & Joshi (1963) expressed the strain energy of the electron gas by eq. (1). This expression gives enormously large values of strain energy and of resulting volume forces at large q, as is obvious from the expression

$$F(r) = -\xi A_q q^2(\alpha_q.\xi)K_e\Omega. \qquad (26)$$

The parameter Θ in this case is a constant equal to unity (see upper horizontal line in figure 2). In order to damp the electron gas effect, the authors committed the mathematical error of squaring the average strain instead of averaging the square of the strain in eq. (1). The average value of the strain in a Wigner-Seitz cell is determined by the compensation of the compressive and dilatational strains and hence gives rise to $G(qr_0)$. On the other hand the strain energy will not exhibit such a compensation when averaged. Thus they obtained an erroneous expression which fortuitously reproduced the correct behaviour of volume forces. The corresponding Θ is given by

$$\Theta = [G(qr_0)]^2 \qquad \ldots \quad (27)$$

and its variation is shown in figure 2.

3.3. *Comparison with the Toya model* (1958)

Volume forces are not calculated in Toya model, but comparing the Fourier transform of the screened effective potential for the electrons (given by eq. (3.1) in Toya (1958) with that of the deformation potential given by eq. (19) in the

present model, one can see that the two numerators are apparently different. However, in the limit of $q \to 0$ the effect of the factor, $|U(r_0) - E_0|$ is negligible and $G(qr_0) \to 1{\cdot}0$ and therefore the two numerators are comparable. At large wave vectors Toya's numerator is much too small because of $G(qr_0)$ while eq (19) is quite large. But the average deformation potential from which the volume forces are calculated in the present model is quite small because of $S(q)$ and hence the result is comparable to that of Toya. The difference in the two denominators is due to the different ways of treating the electron redistribution.

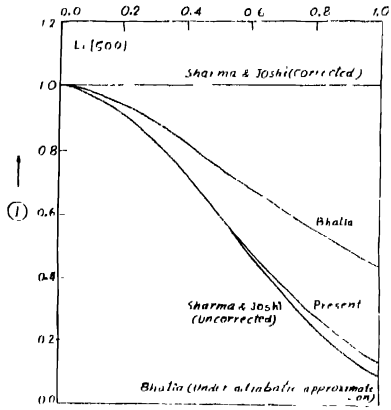

Fig. 2 ζ-dependence of the parameter Θ in [ζ 0 0] direction of lithium for different electron gas models.

3.4 *Limitations*

Toya's model is superior in one respect, viz. it takes account of *Umklapp processes* and hence conforms with the symmetry requirements of the lattice, while the present model does not. Besides the expression for the volume forces has been deduced by minimising the energy of the electron gas at equilibrium (see eq (13)) Similarly one obtains the expression for the force between ions by minimising the energy of the ions at equilibrium Hence this method implies that the lattice is in equilibrium separately under two mechanisms and that the total energy of the lattice exceeds the minimum value even at equilibrium The authors are making attempts to restore the equilibrium condition for the lattice as a whole by associating an additional constant with the electron gas.

4 Conclusions

The present model gives a better and consistent description of volum forces in metals than all the existing ones. It also gives as good results as that of the

pseudopotential method The model is based on Thomas-Fermi and deformation potential approximations and is therefore strictly valid for lattice vibrations of small wave vectors. Nevertheless, by the time errors become appreciable at large wave vectors, the interference factor, $S(q)$ comes to its rescue and reduces the magnitude of the volume forces to very small values. Inspite of this, the model does not satisfy the symmetry requirements of the lattice. However, this deficiency can be corrected for by using Bloch wave functions instead of simple sinusoidal functions to represent electrons.

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